Supporting information

Facile Solvent-Free Mechanochemical Synthesis of UI_3 and Lanthanoid Iodides

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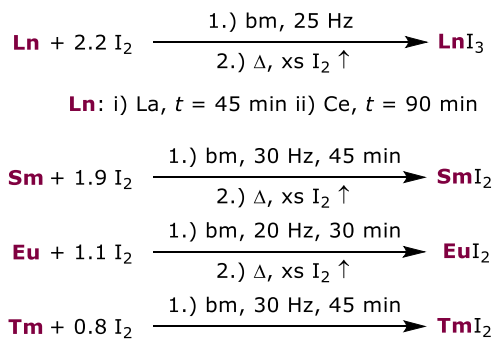
Detailed experimental procedures

General: Compounds were manipulated under an inert argon atmosphere using typical Schlenk line and glovebox (MBraun, O_2/H_2O : > 0.1 ppm) techniques. Rare-earth metals (> 99.9 % purity) were purchased as small pieces from either ChemPur or Smart elements and were either filed or cut into small pieces prior to use (We recommend purchasing pre-cut metal from Smart Elements as a supplier, as other commercial suppliers often provide the rods or chunks in oil, or with a significant amount of oxide coating. When using a rod, ensure that the material is cut cleanly, or filed with a diamond file to avoid Fe contamination from iron files). Iodine was purchased from Sigma-Aldrich and was quickly degassed prior to use. The oscillating ball mill apparatus was purchased from Retsch (400 MM), along with the milling containers (inner layer being either tungsten carbide or steel in 15 or 25 mL volume). Powder X-ray diffraction was performed using a P-XRD Stoe Stadi-P equipped with a Mythen 1 K detector and measured from 0 to 60° in 1° steps and 120 s exposure time in Debye-Scherrer geometry using Mo-Kα_1 radiation.

General ball milling considerations to ensure high yields and short reactions times for lanthanoid and actinoid iodides:

1. A tungsten carbide container is necessary, as the analogous synthesis in a steel mill appeared to give alternative products.
2. In the instance where an excess of metal is used: if metal chunks (e.g. chips) are used these can be removed through a metal sieve after reaction.
3. In the instance of using excess iodine and non-granulated lanthanoid metal (e.g. chips): prior to the actual mechanochemical reaction it is recommended to mill the mixture at 16 Hz for approximately 20-30 minutes to break up the metal pieces. By milling at 16 Hz for this duration, no indication of a reaction was observed when the container was opened.
4. If the metal used is dull (e.g. with an oxide coating), an excess of iodine is recommended along with longer reaction times.
5. The size of the milling container must be considered, targeting large amounts of product requires a larger container. For the lighter lanthanoids a 15 mL container is appropriate for a targeted yield of about 2.0 g. For the heavier lanthanoids a targeted yield of < 1.5 g is advisable.
6. Avoid using an overly large excesses of iodine; this appears to hinder the overall obtained yield of the product.
7. Ensure that the container is sealed tight (preferably with a band of Teflon tape around the screw) to avoid loss of material through potential leaks.

Remarks: Although the synthesis of LnI_3 for the lighter lanthanoids were successful, the procedure was less efficient for the heavier lanthanoids, which required longer reaction times and for Dy a higher frequency was necessary (30 Hz, as minimal reaction occurred at 25 Hz). Furthermore, for both Tm and Lu the reaction was poor, also requiring a higher frequency (no reaction occurred at 25 Hz), very long reaction times with intermittent heating (at 150 °C) between milling cycles, and only gave poor (TmI_3: 35%) to moderate yields (LuI_3: 56%), where for Lu there was still unreacted Lu metal present. The observation for the poor synthesis of TmI_3 is surprising, especially after the synthesis of TmI_2 was successful under milder conditions. It suggests that the ratio of metal to iodine has a substantial influence on the reactivity of the heavier elements – where contrary to what is expected more iodine inhibits reactivity. To this effect, when a 1:1 ratio of Ln (Tm or Lu) to I_2 is first milled, followed by the addition of half an equivalent of I_2, TmI_3 in obtained in 93% yield, and LuI_3 in 77% yield in a lower time and lower frequency (25 Hz). Table 1 provides an overview over the conditions for all syntheses described herein.



Scheme S1. Details for the syntheses of LnI_3 (Ln = La, Ce) and LnI_2 (La = Sm, Eu, Tm).

Table S1. Milling conditions for the one pot, one time synthesis of lanthanoid di- and triiodides.

Metal	I_2 (m)	Oscillation (Hz)	Time (min)	Product	Yield (%)
Samarium	~1[a]	25	99	SmI_2	71[b]
Europium	1.1[c]	20	50	EuI_2	76
Thulium	0.8	25	99	TmI_2	98
Ytterbium	~1[a]	25	99	YbI_2	96
Lanthanum	1.7	25	60	LaI_3	84
Cerium	1.7	25	90	CeI_3	76
Neodymium	1.6	25	99	NdI_3	78
Gadolinium	1.7	25	120	GdI_3	72
Terbium	1.5	25[d]	198	TbI_3	70
Dysprosium	1.6	30	190	DyI_3	85
Thulium	1.5	30	315	TmI_3	35
Lutetium	2.4	30	615	LuI_3	56

[a] a slight excess (< 5%) of metal was used to maintain reducing conditions; [b] after oscillation, excess metal was separated by passing the contents through a metal sieve; [c] for europium no further oxidation (EuI_3) occurs in the presence of excess iodine, excess I_2 is removed post-reaction; [d] material was heated after reaction.

Synthesis of europium(II) iodide

Method a) Under an argon atmosphere, europium metal (0.526 g, 3.46 mmol), iodine pellets (0.999 g, 3.94 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (25 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was oscillated at 20 Hz for 50 minutes. Afterwards, the container was transferred back into the glove box and opened, revealing a light brown powder (Figure S3, *left*). The material was transferred into a Schlenk flask and under reduced pressure light heating was applied (~120 °C, supplied by a temperature controlled heat gun), removing the excess I_2 leaving a pale-yellow powder (Figure S3, *right*). Subsequent powder X-ray diffraction analysis of the material indicated the formation of EuI_2.Yield: 1.13 g (76 %).

Figure S1. Pictures relating to the synthesis of EuI_2. *Left*: colour of the material from the container indicating excess iodide is present (brown colour); *Right*: after removal of iodine by heating and exposing to vacuum.

Synthesis of lanthanum(III) iodide

Method a: Under an argon atmosphere, lanthanum metal (0.556 g, 4.00 mmol), iodine pellets (1.117 g, 4.40 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (25 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was oscillated at 25 Hz for 45 minutes. Afterwards, the container was transferred back into the glove box and opened, and more iodine was added (1.111 g, 4.38 mmol), the mixture was milled for an additional 10 minutes at 25 Hz. After reaction, the jar was transferred to the glovebox and opened revealing a dark brown powder. The material was transferred into a Schlenk flask (Figure S5, *left*), and under reduced pressure light heating was applied (~120 °C, supplied by a temperature controlled heat gun), removing the excess I_2 leaving a colourless powder. The powder was transferred to a small vial (Figure S5, *right*), and subsequent powder X-ray diffraction analysis of the material indicated the formation of LaI_3.Yield: 1.164 g (56 %).

Figure S2. Pictures relating to the synthesis of LaI_3 (Method A). *Left*: colour of the material from the container indicating excess iodide is present (brown colour); *Right*: after removal of iodine by heating and exposing to vacuum and transfer to a small vial.

Method b: Under an argon atmosphere, lanthanum metal (0.600 g, 4.32 mmol), iodine pellets (1.83 g, 7.20 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape), and transferred to the ball mill apparatus and was oscillated at 25 Hz for 60 minutes. The resulting brown powder was transferred to a Schlenk flask after filtration through a metal sieve (to remove large chunks), and exposed to vacuum with heat supplied by a heat gun. After several minutes the iodine was removed leaving a off-white powder (Figure S5.1). Yield 1.90 g (84 %).

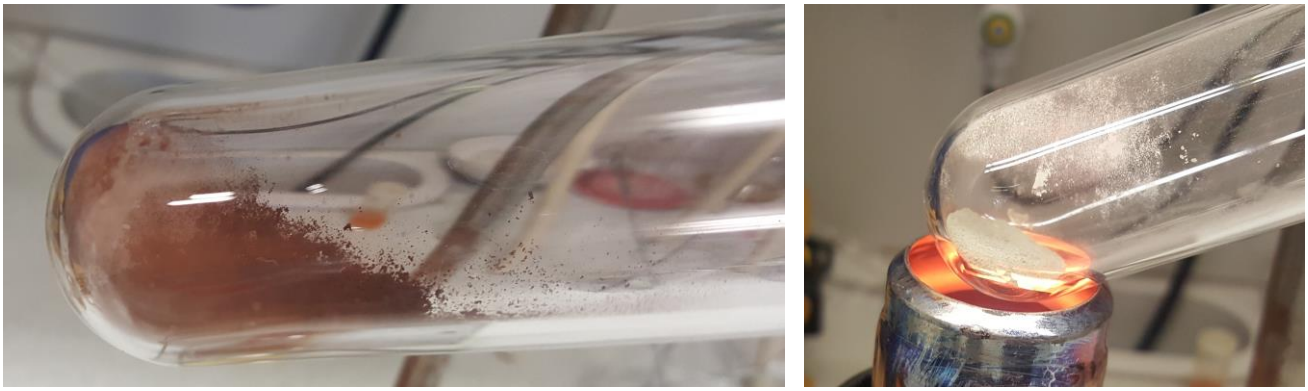


Figure S2.1. Pictures relating to the synthesis of LaI_3 (Method B). *Left*: colour of the material from the container indicating excess iodide is present (brown colour); *Right*: after removal of iodine by heating and exposing to vacuum.

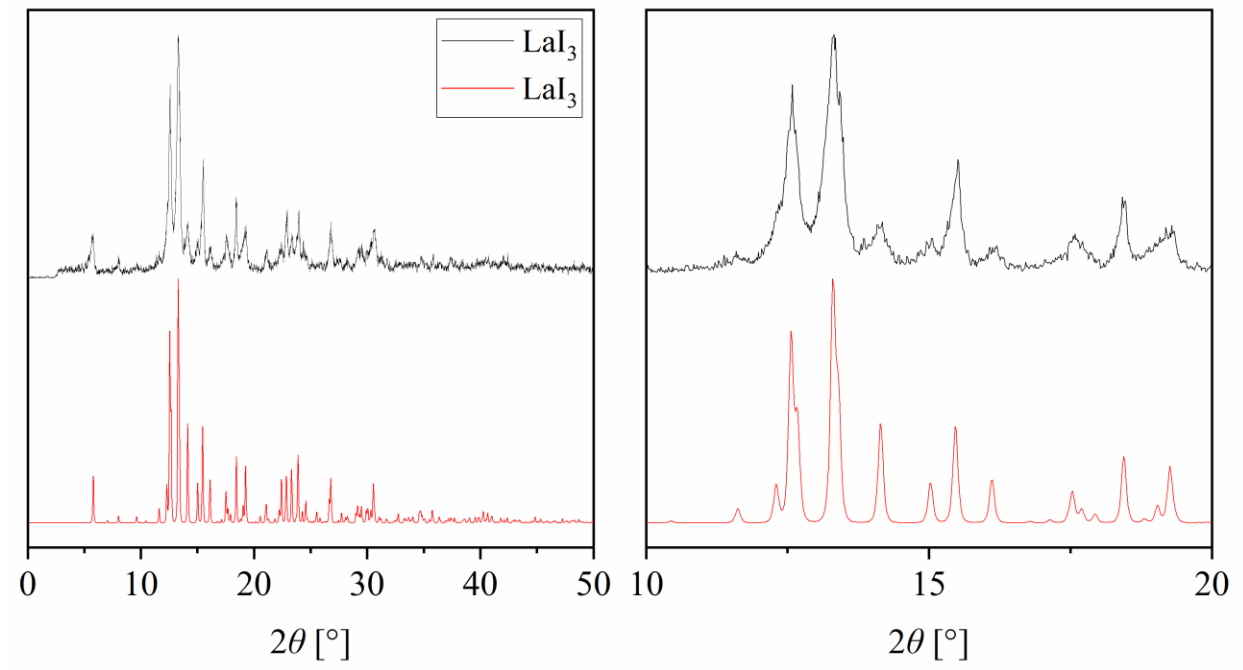


Figure S2.2. Powder diffractogram of LaI_3, with the measured (black) and calculated theoretical (red) pattern.

Synthesis of cerium(III) iodide

Under an argon atmosphere, cerium metal (0.411 g, 2.93 mmol), iodine pellets (1.286 g, 5.07 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (25 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was oscillated at 25 Hz for 90 minutes. Afterwards, the container was transferred back into the glove box and opened, revealing a brown powder. The material was transferred into a Schlenk flask and under reduced pressure light heating was applied (~120 °C, supplied by a temperature controlled heat gun), removing the excess I_2 leaving a light yellow powder (Figure S6). Subsequent powder X-ray diffraction analysis of the material indicated the formation of CeI_3.Yield: 1.129 g (76 %).

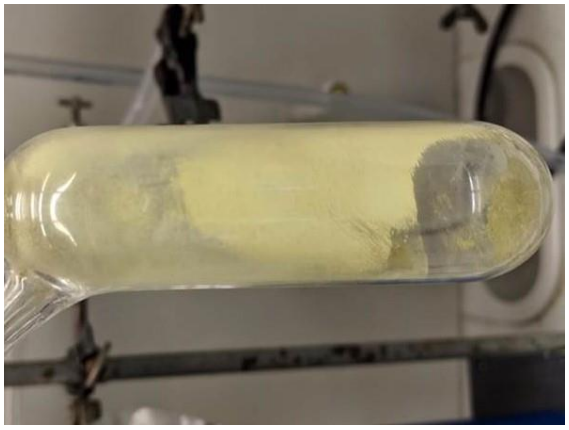


Figure S3. Picture relating to the synthesis of CeI_3, namely the colour of the material after the removal of iodine by heating and exposing to vacuum.

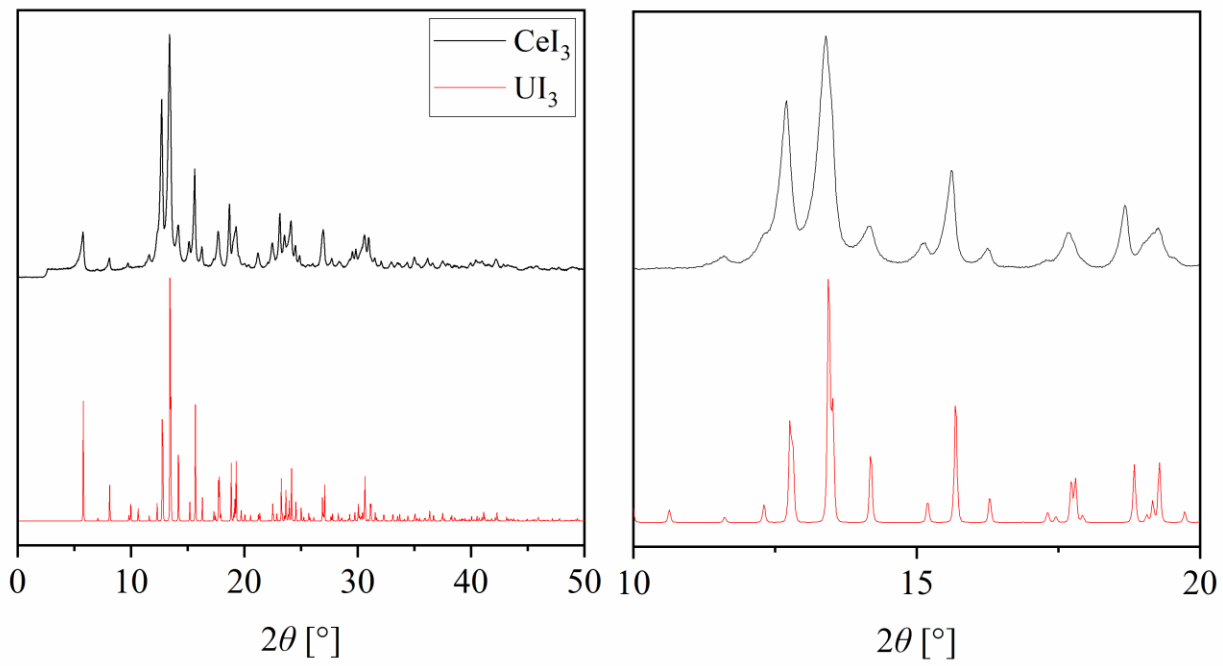


Figure S3.1. Powder diffractogram of CeI_3, with the measured (black) and calculated theoretical (red) pattern based on the isostructural UI_3.

Synthesis of uranium(III) iodide

3.51 g (14.7 mmol) uranium metal and 5.6 g (22.1 mmol, 1.5 eq) iodine were added to a milling vessel (steel, 10 ml, 2 milling balls). This was submerged into liquid nitrogen until the boiling stopped. The cooled milling vessel was inserted into the oscillating ball mill and was milled at 30 Hz for 30 min, while it warmed up to room temperature. A sample of the mixture was taken and the process repeated for another two times. Afterwards the process was repeated another three times, with a sample taken every 60 minutes.

Visual inspection of the samples after two hours showed no reaction. The mixture still contained coarse particles of uranium metal. After 150 min the material became finer, showing an almost black colour.

Samples taken after 180 min and 240 min showed an even finer, black-greyish powder. After 300 min and 360 min the powder was uniform, jet-black, and very fine. PXRD revealed that no reaction had taken place though.

Samples taken after 150 min, 180 min, 300 min and 360 min were thus taken, pressed into a pellet, sealed into a quartz ampoule and treated at 500 °C, while heating from room temperature to 500 °C for 12 h, holding the temperature for 12 hours and cooling for 72 hours. Figure S14 shows the samples after temperature treatment.

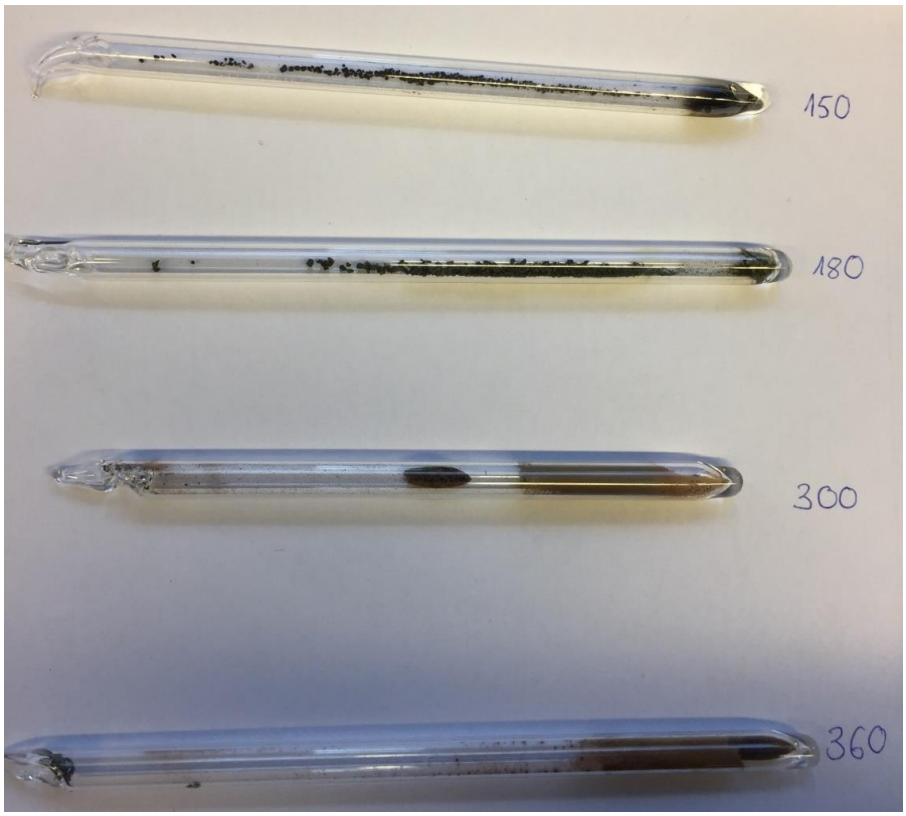


Figure S4. Ampoules of mixtures of U and 1.5 eq I_2 after 150, 180, 300 and 360 min of ball milling followed by temperature treatment at 500 °C.

The samples which were milled for 150 or 180 min respectively did not yield any UI_3 after temperature treatment at 500 °C. Figure S15 shows the content of the ampoules which contain coarse, grainy material which is in stark contrast to jet-black needle-like crystals of UI_3.

Figure S5. Unreacted mixtures of U and 1.5 I_2, which were milled for 150 (left) and 180 (right) min prior to temperature treatment at 500 °C.

In contrast, samples taken after 300 min and 360 min and which were treated at 500 °C showed the successful formation of UI_3 as analysed by PXRD (Figures S16 and S17).

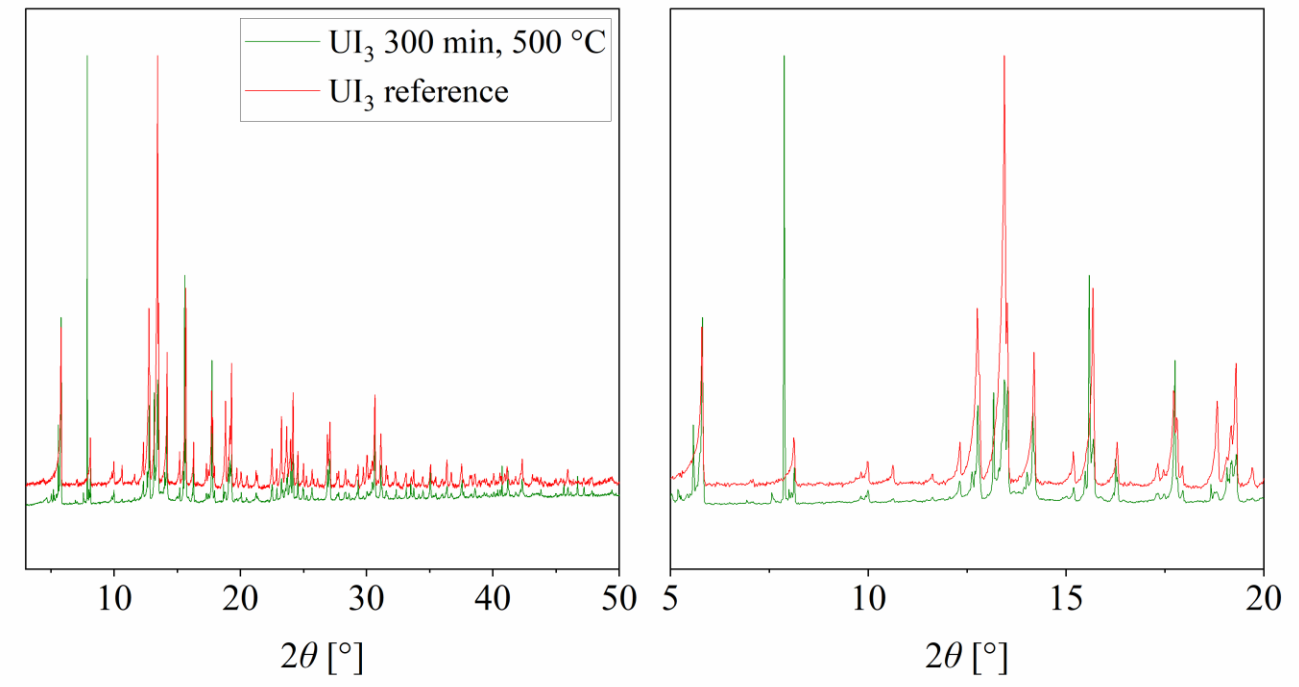


Figure S6. PXRD of sample taken after 300 min of milling at 30 Hz and subsequent temperature treatment at 500 °C showing the reflections of UI_3 (green) that compare well with a reference sample (red).

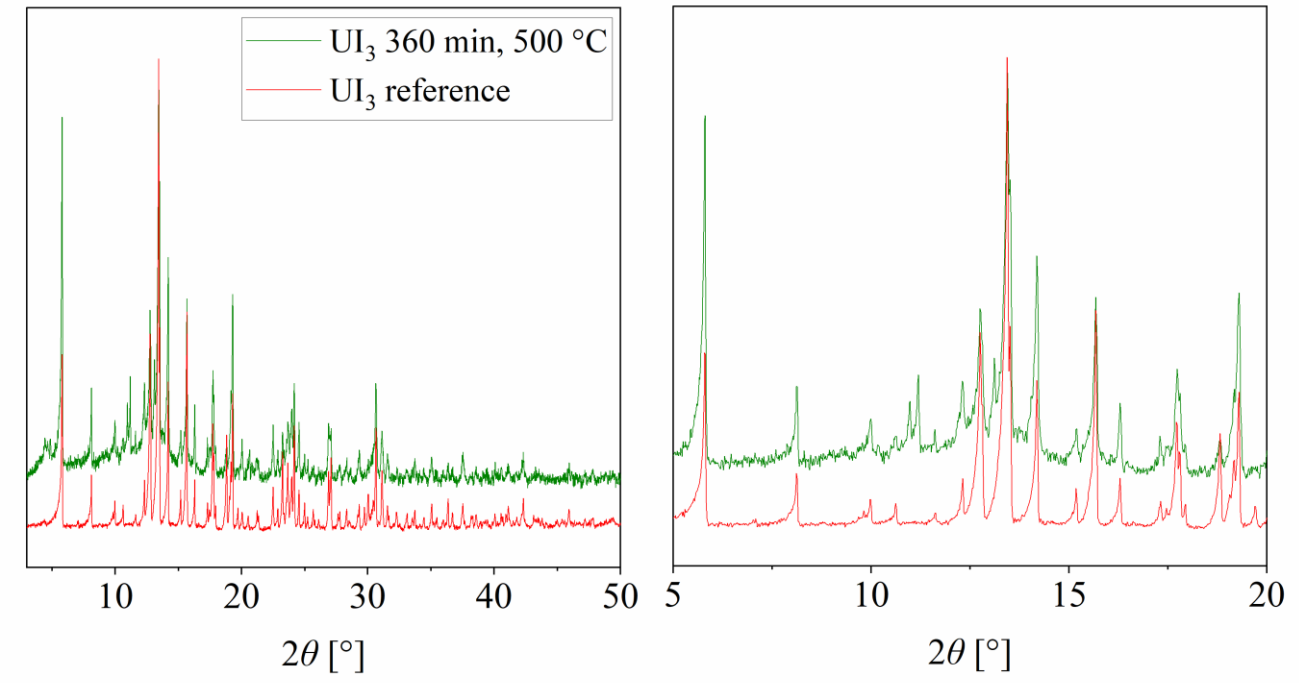


Figure S7. PXRD of sample taken after 360 min of milling at 30 Hz and subsequent temperature treatment at 500 °C showing the reflections of UI_3 (green) that compare well with a reference sample (red).

In another step we tried to identify the lowest possible temperature at which a reaction takes place. For this, three samples containing altogether 400 mg of material were taken (each milled at 30 Hz for 6 x 60 min according to the procedure described above), pressed into a pellet, flame sealed into an ampoule and treated at 150 °C (by placing it into the drying oven) 225 °C, 300 °C and 400 °C, respectively, by using a heat – dwell – cool cycle of 12 h – 12 h – 24 h.

After temperature treatment the sample at 150 °C and 225 °C have not changed at all. The samples at 300 °C and 400 °C showed jet-black crystals. PXRD showed that temperatures of 150 °C and 225 °C are not high enough for the powdered mixture to react off to UI_3. In contrast, UI_3 formation was observed at both 300 °C and 400 °C.

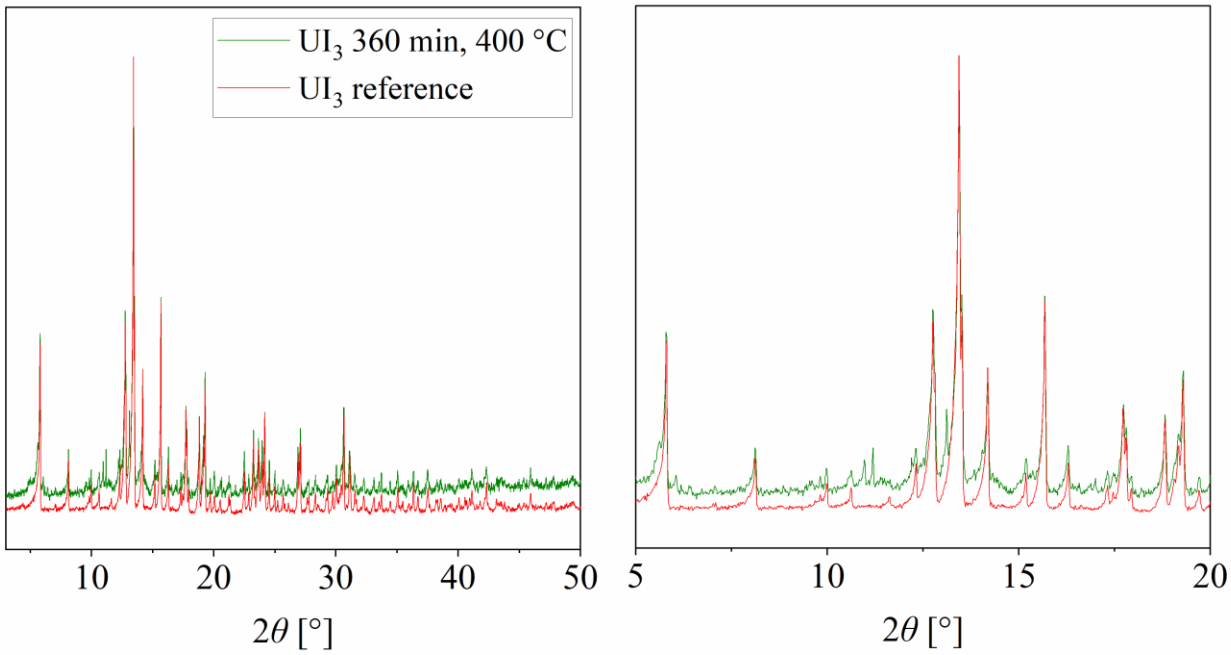


Figure S8. PXRD of sample taken after 360 min of milling at 30 Hz and subsequent temperature treatment at 400 °C showing the reflections of UI_3 (green) that compare well with a reference sample (red).

In one batch that was milled for altogether 360 min and treated at 500 °C by using a heat – dwell – cool cycle of 12 h – 12 h – 12 h very large crystals of UI_3 were obtained (Figure S19).

Figure S9. Large UI_3 crystals after temperature treatment at 500 °C of material that was milled for 360 min.

In further experiments with the steel milling vessel we noticed the formation of very fine, thin, cobweb-like light brown crystals, which we attributed to the formation of iodides of iron or other metals present in the stainless steel alloy of the milling vessel. Due to the hardness of the uranium metal we hypothesised that abrasions on the inner surface, in addition to cleaning procedures outside the glove-box and exposure to air and moisture may ultimately give rise to slow corrosion and may cause the formation of unintended side products. We could not further identify the material precisely, neither by PXRD nor SEM, so we switches to tungsten carbide (WC) as the milling vessel.

The treatment of the material proceeded in a similar fashion as described above, apart from the cooling to -196 °C (this may cause the milling vessel to break from thermal stress).

However, uranium metal is so hard that its abrasive effects were even prominent on the WC. After the isolated UI_3 was dissolved in organic solvents and removed for other experiments, we noticed a residual dark grey powder. Upon investigation with PXRD we were able to confirm that this was indeed WC (Figure S20).

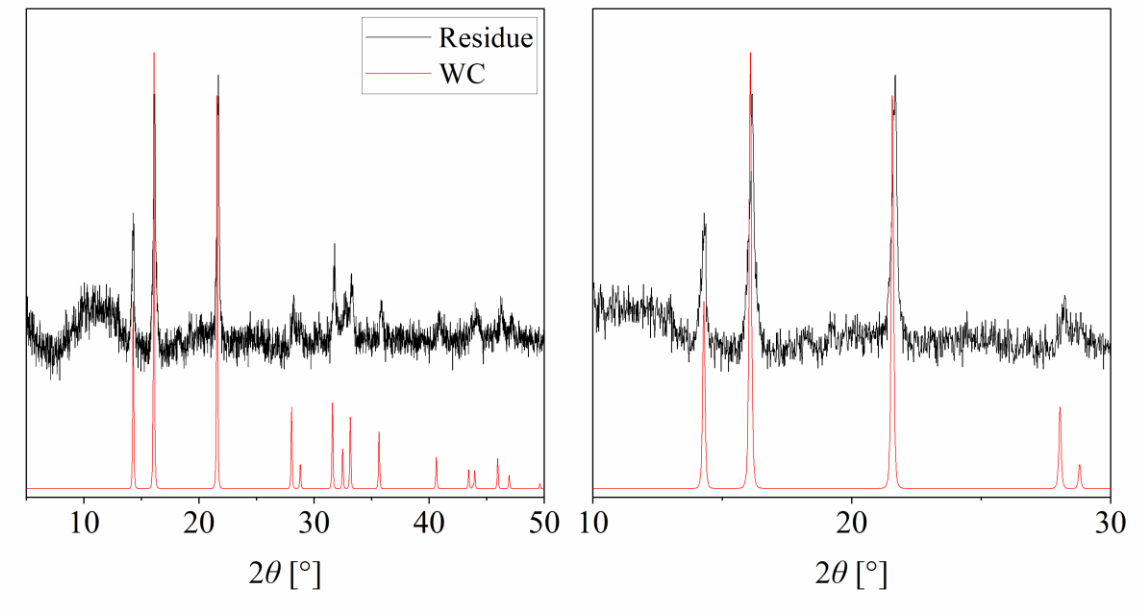


Figure S10. PXRD of insoluble residue confirming the presence of WC abrasions.

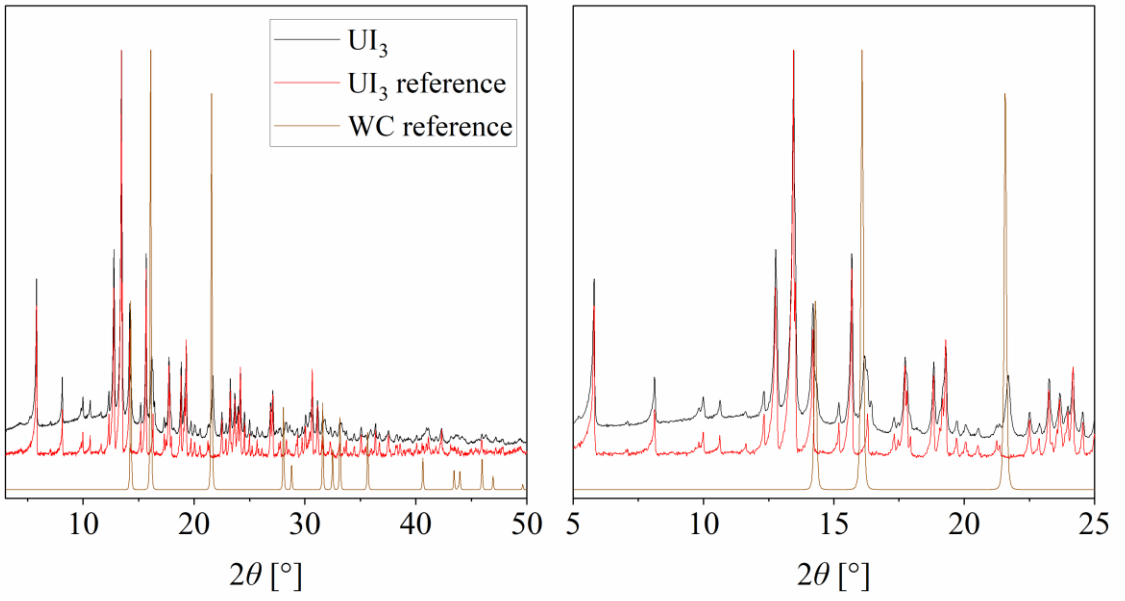


Figure S11. Full scale diffractogram of UI_3 synthesised from ball milling in a WC mill along with WC abrasions.

We further investigated different heating cycles as to whether the crystal growth could be influenced. In our hands, this was not successful. We continued to press the material into a pellet and flame-seal this into an ampule and subject it to 500 °C, but using a heat – dwell – cool program of either 3 – 12 – 57 h or 3 – 0 – 69 h did not result in different crystal growth. The former resulted in a jet-black pellet with tiny crystallites on its surface, whereas the latter produces a rough pellet with a dark grey appearance (Figure S22). Both materials were confirmed to be UI_3 according to PXRD.

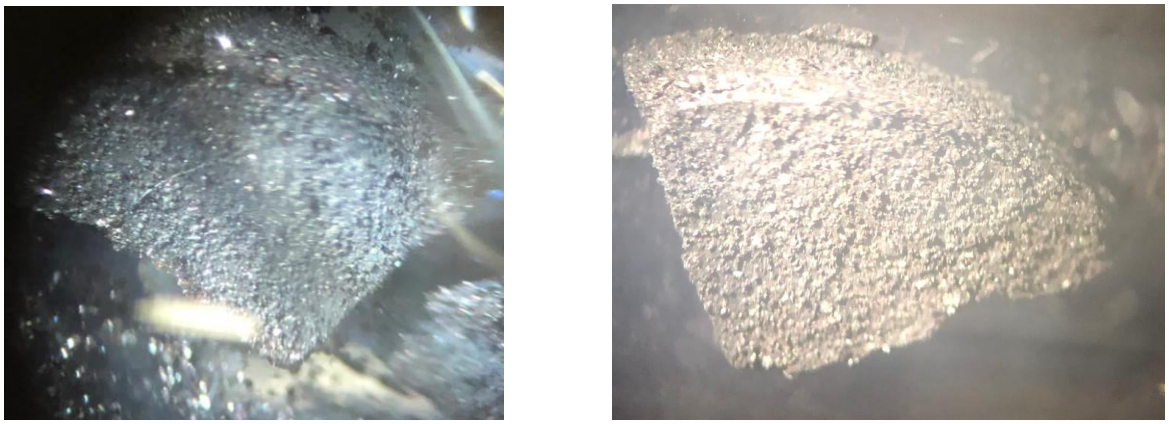


Figure S12. Jet-black UI_3 pellet with tiny crystallites on its surface crystals (left) and grey UI_3 pellet with rough surface (right) after temperature treatment at 500 °C on a 3 – 12 – 57 h (left) and 3 – 0 – 69 h (right) cycle of material that was milled for 360 min in a WC milling vessel.

Further experiments with alternated heating and cooling times also did not improve crystallisation in this case (6 – 12 – 54, 12 – 12 – 48 and 18 – 12 – 42 h cycles), and seem to be – at least in our hands – a matter of chance. Having only a tubular furnace with one heating zone may be one of the reasons for this. If the pellet breaks up upon transfer into the ampoule may also impact the crystallinity of the final product. Regardless of crystallinity though, the material is of sufficient purity and quality for further syntheses.

Additional experiments

To probe the understanding of the mechanosynthetic method for lanthanoid iodides, preliminary investigations were performed. Below is a summary of the observations and any problems we observed for each material.

Synthesis of lanthanoid(II) iodides

Samarium(II) iodide

Under an argon atmosphere, samarium metal (0.472 g, 3.14 mmol), iodine pellets (0.790 g, 3.11 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was transferred to the ball mill apparatus and was oscillated at 25 Hz for 99 minutes. Afterwards, the container was sealed (with additional Teflon tape) and transferred back into the glove box and opened, revealing a deep dark green powder. The powder was filtered through a sieve (Figure S1, *left*) removing any excess metal or larger chucks of material (in total 0.20 g), and the remaining fine material was transferred into a small reaction vial. Yield: 0.870 g (71 %, Figure S1, *right*). Exposure of the dark green powder to air produced a light yellow material. *Note*: The reaction proceeds better when it is performed in an emptied (but not cleaned) milling jar from a previous SmI_2 synthesis.

Figure S13. Pictures relating to the synthesis of SmI_2. *Left*: removing large chunks of material from the reaction and separating it; *Right*: fine particulate material of SmI_2.

Ytterbium(II) iodide

Under an argon atmosphere, ytterbium metal (0.470 g, 2.72 mmol), iodine pellets (0.680 g, 2.68 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed and transferred to the ball mill apparatus and was oscillated at 25 Hz for 99 minutes. Afterwards, the container was transferred

back into the glove box and opened, revealing a light yellowish-green powder (Figure S2). The material was transferred into a small reaction vial. Yield: 1.10 g (96 %).

Figure S14. Pictures relating to the synthesis of YbI_2 showing the green/yellow colour of YbI_2.

Thulium(II) iodide

Method a, large excess of metal un-tempered: Under an argon atmosphere, thulium metal chips (0.530 g, 3.14 mmol), iodine pellets (0.64 g, 2.52 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was oscillated first at 16 Hz for 30 minutes (to granulate the Tm metal), followed by 25 Hz for 99 minutes. Afterwards, the container was transferred back into the glove box and opened revealing a dark grey - dark brownish powder. The powder was filtered through a metallic sieve (Figure S4, *left*). Yield 1.04 g (98%). A small amount of un-tempered powder was treated with THF revealing a dark green solution (Figure S4, *middle*), with a dark grey powder (Figure S4, *right*).

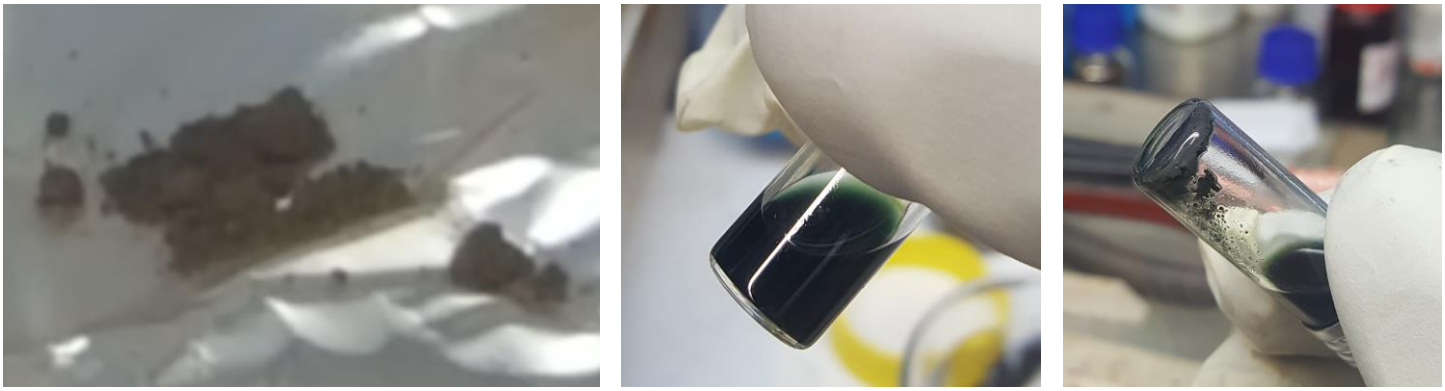


Figure S15: Pictures relating to the synthesis of TmI_2. *Left*: colour of the material from the container, after filtering from metal sieve. *Middle*: dissolved in THF. *Right*: dark grey material in THF.

Method b, large excess of metal: Under an argon atmosphere, thulium metal chips (0.622 g, 3.23 mmol), iodine pellets (0.73 g, 2.88 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was oscillated first at

16 Hz for 30 minutes (to granulate the Tm metal), followed by 25 Hz for 99 minutes. Afterwards, the container was transferred back into the glove box and opened revealing a dark grey - dark brownish powder (Figure S4.1). 1.30 g of material was then separated into three separate vials, one vial was filtered through a metal sieve and tempered under vacuum at 500 °C, the other unfiltered and tempered under vacuum at 500 °C for 24 hours.

Figure S15.1: Pictures relating to the synthesis of TmI_2. *Left*: colour of the material from the container, prior filtering. Shining pieces are pieces of metal.

Method c, small excess of metal: Under an argon atmosphere, thulium metal chips (0.584 g, 3.46 mmol), iodine pellets (0.85 g, 3.35 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was oscillated first at 15 Hz for 30 minutes (to granulate the Tm metal), followed by 25 Hz for 99 minutes. Afterwards, the container was transferred back into the glove box and opened revealing a light brown/yellow powder (Figure S4.2. The powder was filtered through a metallic sieve, giving 1.10g of powder.

Figure S15.2: Pictures relating to the synthesis of TmI_2 with a near stoichiometric degree of Tm to iodine. *Left*: colour of the material from the container.

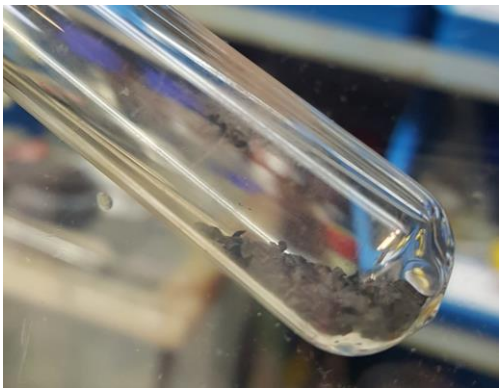
Synthesis of lanthanoid(III) iodides

Neodymium(III) iodide

Method a, large scale: Under an argon atmosphere, Neodymium metal (1.07 g, 7.41 mmol), iodine pellets (2.800 g, 11.03 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was then oscillated at for a few minutes at 25 Hz. It became evident that the ball was wedged within the chamber due to overpacking. The container was then stored in a 140 °C oven for 15 minutes and immediately milled for 20 minutes at 25 Hz. Within the glovebox the ampule was opened and amongst the brown powder was both Nd metal and iodide crystals. Fresh Iodine was added (0.200 g, 0.79 mmol) and the container was re-milled for an additional 40 minutes at 25 Hz. Afterwards, the resulting brown powder was transferred to a Schlenk flask and the excess iodine was removed through heating under reduced pressure. The resulting green powder obtained (1.30 g, 33 %) contained large chunks of unreacted Nd metal (Figure S7).

Figure S16. Pictures relating to the synthesis of NdI_3. Colour of the material after the removal of iodine by heating and exposing to vacuum. Large chunks were resulting neodymium chips were identified (blue circle).

Method b: Under an argon atmosphere, neodymium metal (0.386 g, 2.67 mmol), iodine pellets (1.08 g, 4.28 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was then oscillated at for 20 minutes minutes at 16 Hz followed by 99 minutes at 25 Hz. The container was brought into the glove box revealing a brown powder. The excess iodine was removed by heating under reduced pressure leaving a green material. Yield 1.10 g (78%).



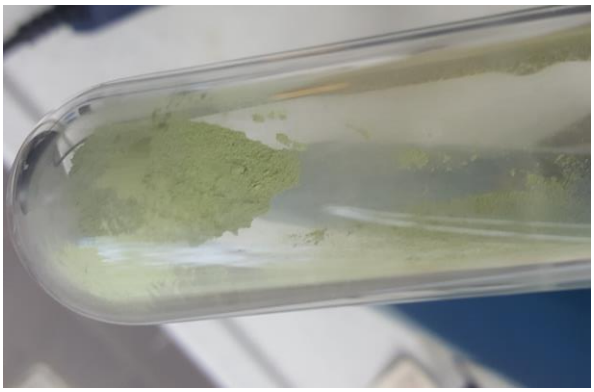


Figure S16.1 Pictures relating to the synthesis of NdI_3. Left: Nd metal with a dull coating. Right: colour of material after milling.

Gadolinium(III) iodide

Under an argon atmosphere, gadolinium metal (0.430 g, 2.73 mmol), iodine pellets (1.200 g, 4.73 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (25 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was then oscillated at 25 Hz for 120 minutes. Afterwards, the container was transferred back into the glove box and opened, revealing a brown powder (Figure S8, left). The material was transferred into a Schlenk flask and under reduced pressure light heating was applied (~180 °C, supplied by a temperature controlled heat gun), removing the excess I_2 leaving a colourless powder (Figure S8, right).Yield: 1.064 g (72 %).

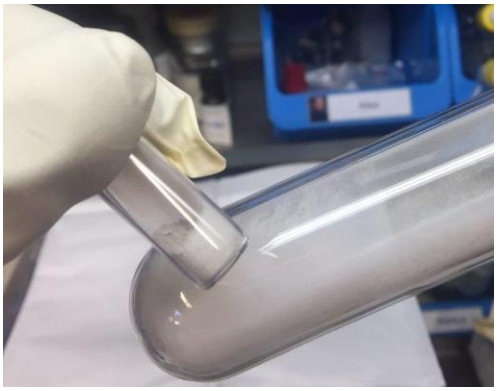


Figure S17. Pictures relating to the synthesis of GdI_3. *Left*: colour of the material in the ball mill. *Right*: colour of the material after the removal of iodine by heating and exposing to vacuum.

Terbium(III) iodide

Under an argon atmosphere, terbium metal (0.357 g, 2.24 mmol), iodine pellets (0.87 g, 3.43 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and transferred to the ball mill apparatus and was then oscillated at for 20 minutes at 16 Hz, prior 99 minutes at 25 Hz. The container was then stored at 150 °C for 30 minutes prior to transference into the glovebox. Upon opening a brown powder was observed. Fresh I_2 (0.100 g, 0.39 mmol) was added and the sample was re-milled at 25 Hz for 99 minutes. Open opening the milling jar and extraction of the off-white material. Yield 0.84 g (70 %).

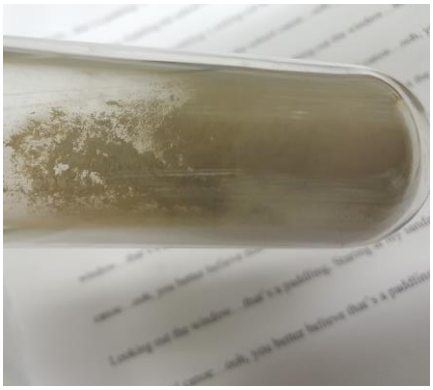


Figure S18. Pictures relating to the synthesis of TbI_3. Colour of the material after the removal of iodine by heating and exposing to vacuum.

Dysprosium(III) iodide

Under an argon atmosphere, dysprosium metal (0.212 g, 1.30 mmol), iodine pellets (0.54 g, 2.13 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and inserted into the ball mill apparatus, and was then oscillated at 30 Hz for 190 minutes. Afterwards, the container was transferred back into the glove box and opened, revealing a brown powder. The material was transferred into a Schlenk flask (Figure S10, *left*), and under reduced pressure light heating was applied (~120 °C, supplied by a temperature controlled heat gun), removing the excess I_2 leaving a pale grey powder (Figure S10)..Yield: 0.60 g (85 %).

Figure S19. Pictures relating to the synthesis of DyI_3. *Left*: dark brown material after milling. *Right*: Light grey material after the removal of iodine by heating and exposing to vacuum.

Erbium(III) iodide

Under an argon atmosphere, erbium metal (0.430 g, 2.57 mmol), iodine pellets (0.97 g, 3.82 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and inserted into the ball mill apparatus, and was then oscillated at 16 Hz for 30 minutes, followed by milling at 25 Hz for 99 minutes. Afterwards, the container was transferred back into the glove box and opened, revealing a brown/purple material (Figure SX8) with iodine crystallites and metal pieces, indicating the reaction did not proceed to completion. The milling jar was stored in an oven (150 °C) for 30 minutes. More iodine (0.238 g, 0.94 mmol) was added, the reaction jar was sealed and stored within a 150 °C degree oven for 15 minutes, prior milling for 120 minutes at 27.5 Hz. The container was re-inserted into the glove box revealing a brown powder. The metal residue was removed giving 1.0 g of material. (71%)

Figure S20. Pictures relating to the synthesis of ErI_3. *Left*: dark brown material after milling. *Right*: off-white material after the removal of iodine by heating and exposing to vacuum.

Thulium(III) iodide

Method a) using an excess of iodine: Under an argon atmosphere, thulium metal (0.400 g, 2.37 mmol), iodine pellets (0.900 g, 3.55 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and inserted into the ball mill apparatus and was then oscillated at 16 Hz for 20 minutes, followed by 25 Hz for 99 minutes. The material was transferred into the glovebox and opened revealing a black / purple material indicating the presence of iodine and no reaction. The material was further milled at 30 Hz for 99 minutes followed by storage at 150 °C for 30 minutes. This was repeated twice. A dark brown material was extracted from the milling container, and the excess iodine was removed at reduced pressure with heating provided by a heat gun (set to 120 °C), resulting in a light grey off white powder. Yield 0.45 g (35%).

method b) using incremental addition of iodine: Under an argon atmosphere, thulium metal (0.320 g, 1.89 mmol), iodine pellets (0.480 g, 1.89 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and inserted into the ball mill apparatus and was then

oscillated at 16 Hz for 30 minutes, followed by 25 Hz for 69 minutes. The material was transferred into the glovebox and opened revealing a pale brown/off-white material. Fresh I_2 was added (0.240 g, 0.94 mmol), and the material was further milled at 25 Hz for 30 minutes. The container was stored at 150 °C for 30 minutes. The material was transferred into a Schlenk flask and was heated under reduced pressure to remove the additional iodine leaving an off-white/yellow powder.. Yield 0.870 g (93%).

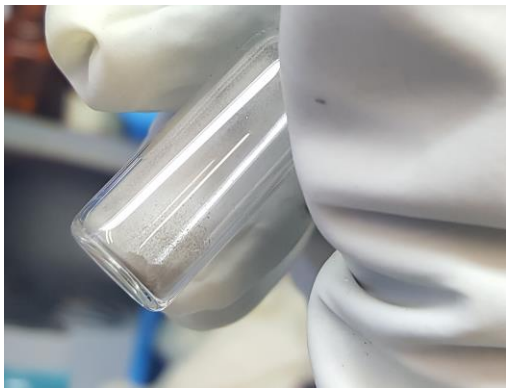


Figure S21. Light off white material of TmI_3 after the removal of iodine by heating and exposing to vacuum.

Lutetium(III) iodide

Method a) using an excess of iodine: Under an argon atmosphere, lutetium metal (0.370 g, 2.11 mmol), iodine pellets (1.06 g, 4.17 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and inserted into the ball mill apparatus, and was then oscillated at 25 Hz for 120 minutes. Afterwards, the container was transferred back into the glove box and opened, revealing a black/purple material indicating the presence of significant amounts of iodine. More iodine (0.238 g, 0.94 mmol) was added, the reaction jar was placed within a 150 degree oven for 10 minutes, prior to milling for 99 minutes at 30 Hz. This procedure was repeated 4 times. Afterwards a brown powder was obtained. The material was transferred into a Schlenk flask (Figure SX8, *left*), and under reduced pressure light heating was applied (~120 °C, supplied by a temperature controlled heat gun), removing the excess I_2 leaving an off white/grey powder. Yield: 0.61 g (52 %).

The following parameters are based on the above synthesis and <u>failed</u> to produce any LuI_3: 1) Lu (0.423 g, 2.4 mmol), I_2 (1.200 g, 4.7 mmol), first heated at 150 °C for 20 minutes followed by immediate milling (30 Hz, 99 minutes), followed by heating at 150 °C for 30 minutes and milling for 30 minutes at 30 Hz, resulting in a dark/purple material and unreacted metal. 2) Lu (0.300 g, 1.7 mmol), I_2 (0.850 g, 3.3 mmol), first heated at 150 °C for 30 minutes followed by immediate milling (30 Hz, 99 minutes). No reaction was observed. Additional I_2 (0.53 g, 2.1 mmol) was added, followed by heating at 150 °C for 45 minutes and milling for 20 minutes at 25 Hz, resulting in a dark/purple material and unreacted metal. The material was again milled for 144 minutes at 30 Hz, resulting in a black/purple material indicating no reaction.

Method b) using incremental amounts of iodine: Under an argon atmosphere, lutetium metal (0.50 g, 2.86 mmol), iodine pellets (0.73 g, 2.87 mmol), and a tungsten carbide milling ball (15 mm diameter), were added to a tungsten carbide milling jar (15 mL). The container was sealed (with additional Teflon tape) and inserted into the ball mill apparatus, and was then oscillated at 16 Hz for 20 minutes followed by 25 Hz for 99 minutes. Afterwards, the container was transferred back into the glove box and opened, revealing a brown powder (Figure S13, left) with some iodine present. The material was milled again at 25 Hz for an additional 99 minutes, and afterwards no indication of free iodine was present. Fresh I_2 (0.40 g, 1.5 mmol) was added followed by milling for 25 Hz for 198 minutes. The container was then stored at 150 °C for 30 minutes. The light brown material was transferred to a Schlenk flask (Figure S13, middle), and excess iodine was removed under reduced pressure with heating at 150 °C from an oil bath. The resulting off-white powder (Figure S13) was identified as LuI_3 by powder X-ray diffraction. Yield: 1.222 g (77%)

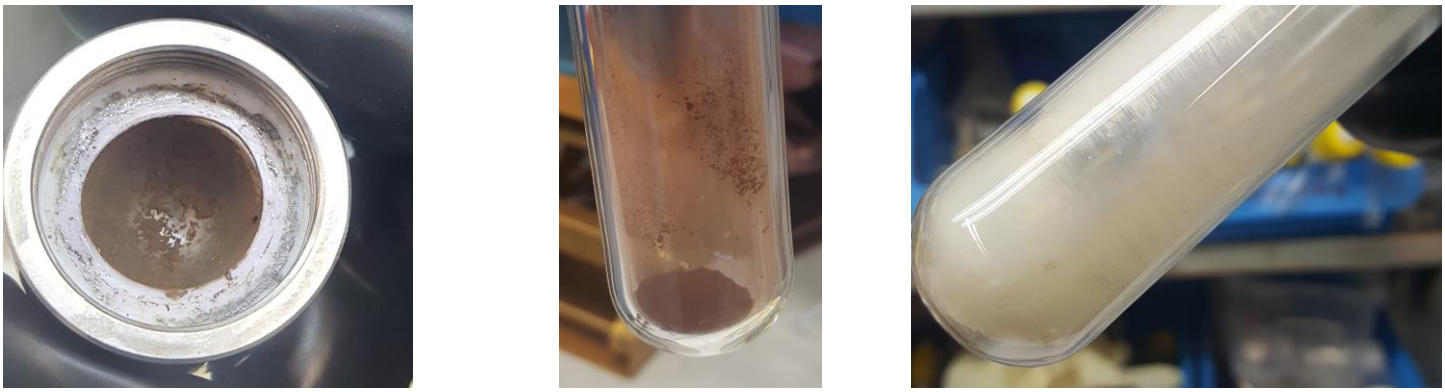


Figure S22. Pictures relating to the synthesis of LuI_3. *Left*: dark brown material after milling prior to addition of more iodine. Middle after milling with excess iodine *Right*: Light off white material after the removal of iodine by heating and exposing to vacuum.

Additional experiments

Synthesis of $[Sm\{N(SiMe_3)_2\}_2]$

SmI_2 (0.570 g, 1.4 mmol prepared by the above method), was added with $KN\{SiMe_3\}_2$ (0.56 g, 2.81 mmol, in slight excess), to the tungsten carbide container with a tungsten carbide ball. The mixture was ossilated at 30 Hz for 115 minutes. Upon opening the chamber, a dark purple powder was obtained. The powder was removed from the ball mill. The dark purple powder (0.770 g), was extracted from the ball mill into a Schlenk Flask and n-Hexane (10 mL) was added. The Schlenk flask was sonicated briefly, and a dark purple solution and white precipitate was obtained. After filtering and evaporation to dryness the remaining purple powder was analysed by ^1H NMR spectroscopy in C_6D_6, indicating the formation of $[Sm\{N(SiMe_3)_2\}_2]$ with minimal remaining $KN\{SiMe_3\}_2$.

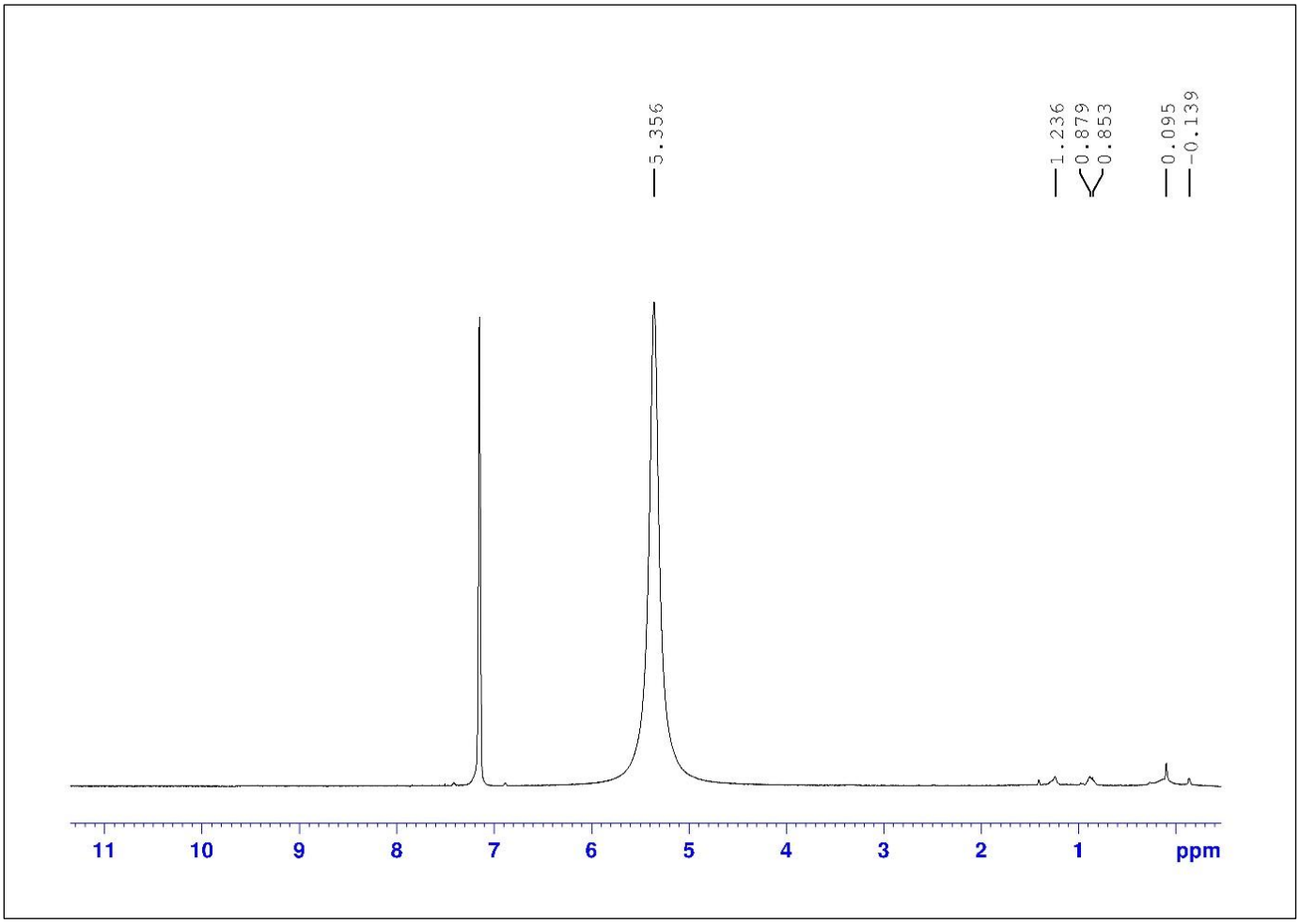


Figure S23. ^1H NMR (C_6D_6, 300 Hz) of dried and isolated $[Sm\{N(SiMe_3)_2\}_2]$.

Synthesis of $[Yb\{N(SiMe_3)_2\}_2]$

YbI_2 (0.259 g, 0.608 mmol prepared by the above method), was added in excess to $KN\{SiMe_3\}_2$ (0.21 g, 1.05 mmol) in a mortar and muddled together giving and olive-green material. The content (0.404 g) was transferred into a tungsten carbide container with a tungsten carbide ball. The mixture was oscillated at 30 Hz for 90 minutes. Upon opening the chamber, an orange powder was obtained. C_6D_6 was added to the chamber, and upon filtration the resulting orange solution was analysed by ^1H NMR spectroscopy in C_6D_6, the formation of $[Yb\{N(SiMe_3)_2\}_2]$ with slight amounts of remaining $KN\{SiMe_3\}_2$.

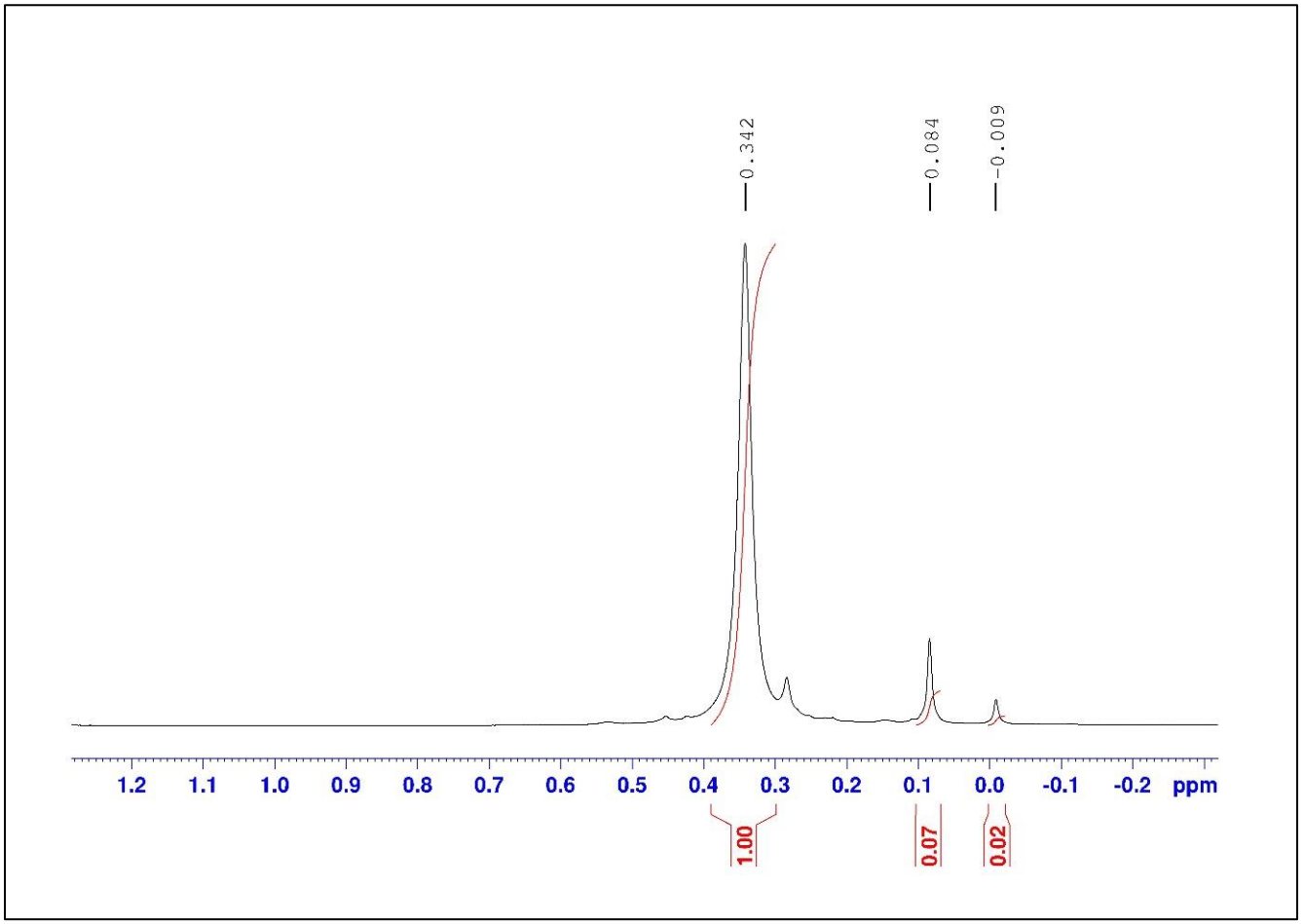


Figure S24. ^1H NMR (C_6D_6, 300 Hz) of a C_6D_6 extract from the reaction between YbI_2 and $KN\{SiMe_3\}_2$ after filtration.

NMR of [U{THF}$_3$]

10 mg (16.2 µmol) of yet-black UI_3 were placed into a Young's tap NMR tube. 1 ml of THF was added to give a dark purple solution. The mixture was dried under vacuum for one hour, before 500 µl of C_6D_6 were added and the ^{1}H-NMR recorded.

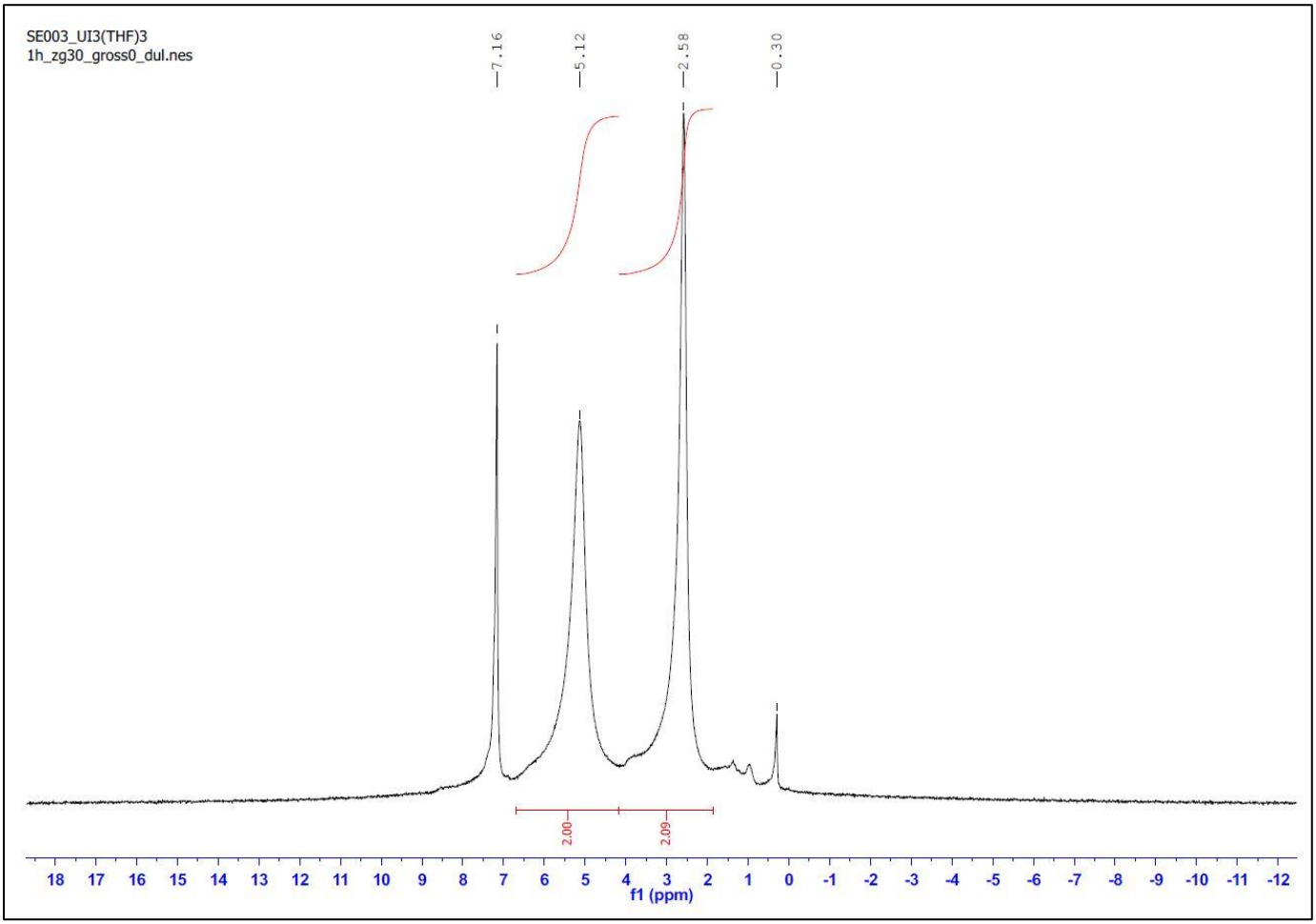


Figure S25. ^{1}H NMR (C_6D_6, 300 Hz) of a C_6D_6 solution of $UI_3(thf)_3$.